

1 TITLE OF THE INVENTION  
2 CEMENTITIOUS COMPOSITIONS AND CEMENTITIOUS SLURRIES  
3 FOR PERMANENTLY PLUGGING ABANDONED WELLS AND  
4 PROCESSES AND METHODS THEREFOR

5 CROSS-REFERENCE TO RELATED APPLICATIONS

6 This application claims the benefit of the priority of  
7 U.S. Provisional Application Serial No. 60/244,330, filed  
8 October 30, 2000 and entitled "CEMENTITIOUS COMPOSITIONS AND  
9 CEMENTITIOUS SLURRIES FOR PERMANENTLY PLUGGING ABANDONED  
10 WELLS AND PROCESSES AND METHODS THEREFOR."

11 BACKGROUND

12 Wells of various types after their useful lives are  
13 shut down and usually permanently plugged for a variety of  
14 reasons. Frequently, depleted hydrocarbon producing wells  
15 are required by laws to be permanently plugged for  
16 protecting aquifers and the above surface environment.

17 Regulations exist for plugging abandoned wells to  
18 protect both below and above surface environments and to  
19 prevent accidents from occurring at the plugged well. Such  
20 regulations often require that the plugs have a certain  
21 minimum strength and maximum liquid permeability.  
22 Governmental agencies often are required to inspect and  
23 approve hydrocarbon well closures before the wells can be  
24 officially certified as closed. For example, in the State  
25 of California the certifying agency is the Department of  
26 Conservation, Division of Oil and Gas.

27 Although approved well-closure compositions exists,  
28 since permanently plugged wells are no longer a source of  
29 income, there is a strong economic incentive to permanently  
30 plug such wells as cheaply as possible. This invention is

1 directed to cheaper cementitious compositions for  
2 permanently plugging wells, processes of preparation of such  
3 compositions, processes for applying such compositions, and  
4 methods having advantages of reducing the costs of such  
5 operations including estimating cost and markup or bid  
6 prices.

7 In the abandonment of hydrocarbon wells, hydraulic  
8 cementitious slurries are used to create hard plugs in the  
9 wellbore which are effective for permanently closing the  
10 well. Specialized equipment is used to inject the slurry  
11 into the well at surface level. Under pressure the slurry  
12 is forced to the bottom of the well and into the  
13 subterranean porosity zone. As the slurry fills in at the  
14 well bottom, sufficient resistance is met to cause the  
15 slurry to lift vertically towards the surface. Based on the  
16 diameter and depth of a given well, the volume of hydraulic  
17 cementitious slurry required to close a particular well can  
18 be calculated. The slurry must produce upon curing a  
19 vertical hard plug to a level of 100 ft. above the  
20 subterranean porosity zone.

21 The performance of a given slurry mix for hydrocarbon  
22 well closure is required to meet the American Petroleum  
23 Institute ("API") specification for a competent hard plug.  
24 As defined by API, a hard plug must meet and maintain a  
25 compressive strength of 1000 psi and have a maximum  
26 permeability of 0.1 millidarcy ("md").

27 Many hydrocarbon production companies contract well  
28 abandonment work to service organizations that specialize in  
29 well closure services. These service organizations use  
30 approved cementitious materials in the slurry mixes for  
31 placing and forming the competent hard plugs. G series  
32 Portland cement and minus 200 sieve silica product ar

1 currently approved materials for well plug slurries. By the  
2 term "silica product" as used herein is meant a solid  
3 material whose major component is silica and is widely used  
4 in hydraulic cements. Generally in such silica products the  
5 amount of silica exceeds about 95% and is usually about 98%  
6 to about 99%. As used herein, the term silica product does  
7 not included cement kiln dust ("CKD"). These materials are  
8 relatively high cost products individually when compared to  
9 the dry cementitious solids of this invention. A typical  
10 silica product suitable for forming hydraulic cementitious  
11 slurries is from about minus 90 mesh silica sand to about  
12 minus 200 mesh silica powder.

13 In current conventional well abandonment operations,  
14 G Series Portland cement is obtained from cement  
15 manufacturers and the silica product from other  
16 manufacturers at other locations. Transportation cost from  
17 two different locations are incurred. Before the cement and  
18 silica product are used to form the hydraulic cementitious  
19 slurry they must be blended, and thereafter slurried with  
20 water, before pumping down the well, as illustrated in  
21 FIG. 1.

#### 22 SUMMARY

23 Accordingly, this invention is directed to less costly  
24 dry cementitious solids for slurry use and a process for  
25 blending such dry cementitious solids which have the  
26 advantage of greatly reducing the cost of hydrocarbon well  
27 abandonment and closing.

28 In general this invention is directed towards dry  
29 cementitious solids comprising cement kiln dust ("CKD") and  
30 cement; hydraulic cementitious slurries produced from such  
31 dry cementitious solids; the solid cementitious compositions

1 resulting from the curing of such hydraulic cementitious  
2 slurries; processes for making and using such materials;  
3 methods of blending the dry cementitious solids prior to  
4 slurring; and methods for estimating and reducing cost and  
5 estimating price markup in well closure operations using the  
6 CKD-containing formulations of this invention.

7 CKD is a waste material generated in cement  
8 manufacture. CKD is a partially calcined kiln feed which is  
9 removed from the gas stream and collected in a dust  
10 collector. Chemical analysis of CKD from cement  
11 manufacturers usually varies depending on the particular  
12 feed. Variations also exist from one manufacture to another  
13 depending in part on the efficiencies of the cement  
14 production operation and the associated dust collection  
15 systems. Typically, the major oxides found in CKD's are  
16  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SO}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . Chemical  
17 analysis of some CKD's are found in U.S. Patent Nos.  
18 4,432,800 and Re.33,747 which are hereby incorporated herein  
19 by reference. Such variations, however, do not have any  
20 detrimental effects on the usefulness and performance of  
21 this invention.

22 CKD is available from a number of cement manufacturers  
23 at a price significantly lower than the cost of materials  
24 currently being used in cementitious slurries for  
25 hydrocarbon well closures. Type II Portland cement is  
26 cheaper than G Series Portland cement by about \$2.00 per ton  
27 based on raw cost. Since the resulting hard cores produced  
28 by this invention using Type II Portland cement meet or  
29 exceed all requirements of API for a competent hard plug,  
30 Type II Portland cement is preferred only for achieving  
31 better economics. Of course, if desired the more expensive

1 G Series Portland cement can also be used. In fact, any  
2 type of cement can be used in this invention.

3 In the economics of hydrocarbon abandonment service  
4 contracts, the profits are determined by a charged cost per  
5 cubic foot ("cf") of slurry, which in turn is determined by  
6 the choice of materials, the transportation cost, and the  
7 blending cost. This invention is also directed to processes  
8 for reducing the cost of well closures.

9 CKD is made available by a number of cement  
10 manufactures so that both the CKD and the cement can be  
11 obtained from the same source essentially at the same source  
12 location thereby reducing transportation cost. CKD is often  
13 regarded as a waste product of the cement industry having  
14 limited use elsewhere.

#### 15 BRIEF DESCRIPTION OF THE DRAWINGS

16 FIG. 1 is a flow diagram for a process for producing a  
17 blended cementitious slurry of cement and silica into an  
18 abandoned well.

19 FIG. 2 is a flow diagram for a process for producing a  
20 hydraulic cementitious slurry formed from a cement-CKD blend  
21 into an abandoned well.

22 FIG. 3 is a flow diagram for a method of determining a  
23 markup price for providing a cement-CKD blend to an off-load  
24 site.

25 FIG. 4 is a flow diagram for a process for producing  
26 and transporting a cement-CKD blend to an off-load site.

27 FIG. 5 is a flow diagram for a process for producing  
28 and transporting a cement-CKD blend to an off-load site and  
29 for closing a well.



1 transportation of the dry cementitious solids will be in the  
2 range of 50 to 100 miles as measured from the cement source  
3 site to the off-load site. Normal vibration generated  
4 during such travel will cause some of the heavier density  
5 cement to work its way down in the container thereby  
6 displacing some of the lighter density CKD and causing the  
7 CKD to rise, thereby blending the materials in the container  
8 automatically while in transit sufficiently for slurring  
9 with water without further blending after off-loading.  
10 Pneumatic off-loadable trucks and railroad cars, for  
11 example, have containers suitable for transportation of such  
12 dry cementitious solids. Just prior to off-loading the dry  
13 cementitious solids the containers are aerated or purged to  
14 remix any concentration of cement in the bed of the  
15 container.

16 In this invention, the blending of CKD and cement,  
17 preferably Type II Portland cement, in specific ratios, when  
18 slurried with water in predetermined amounts, will produce a  
19 variety of slurries that will achieve a compressive strength  
20 at least of 1000 psi and meet or exceed all requirements of  
21 API for a competent hard plug.

22 Accordingly, there is provided by the principles of  
23 this invention, novel cementitious compositions and  
24 hydraulic cementitious slurries using CKD as one of the  
25 major components thereof.

26 In one embodiment of this invention, the cement is Type  
27 II Portland cement, however, any type of cement can be used  
28 if desired.

29 In another embodiment of this invention, the CKD has at  
30 least about 10% free lime as determined by analysis. All  
31 percents herein, unless otherwise specified, are weight

1 percents. By the term "free lime" as used herein is meant  
2 calcium existing in the form of calcium oxide, i.e. CaO.

3 In still another embodiment of this invention, the CKD  
4 has at least about 40% CaO as determined by analysis on an  
5 oxide basis.

6 In one embodiment of this invention, a dry cementitious  
7 composition is provided, which when slurried with water, is  
8 effective for permanently plugging a well. The dry  
9 cementitious composition comprises CKD and cement as the  
10 major components. In a further embodiment, the CKD is at  
11 least about 40% by weight of the dry cementitious  
12 composition. In another further embodiment, the cement is  
13 at least about 40% by weight of the dry cementitious  
14 composition.

15 In another embodiment, the dry cementitious composition  
16 is about 50% by weight CKD, and about 50% by weight cement.

17 In still another embodiment, the dry cementitious  
18 composition is about 60% by weight CKD and about 40% by  
19 weight cement.

20 In one embodiment of this invention, a dry cementitious  
21 composition is provided which comprises cement and CKD as  
22 major components and which also has a weight ratio of parts  
23 of cement to parts of CKD between about 2/3 and 3/1.

24 In further embodiment, the dry cementitious composition  
25 is at least about 70% by weight cement and CKD. In a still  
26 further embodiment, the dry cementitious composition is at  
27 least about 90% by weight cement and CKD.

28 In further embodiment, the dry cementitious composition  
29 has a weight ratio of parts of cement to parts of CKD  
30 between about 2/3 and about 7/3, and preferably between  
31 about 2/3 and about 3/2.



1 In hot wells, to prevent boiling of the hydraulic  
2 cementitious slurry, the slurry can also contain a  
3 predetermined amount of silica flour. Silica flour is fine  
4 silica, generally  
5 about minus 325 mesh.

6 In a further embodiment, the dry cementitious  
7 composition also contains silica flour. In a still further  
8 embodiment, the dry cementitious composition has a weight  
9 ratio of parts of silica flour to parts of cement of from  
10 about 0.30 to about 0.40.

11 In the cement industry, the unit weight of dry cement  
12 and cementitious materials is a "sack." A sack is defined  
13 as 94 lbs. of dry cementitious material. Thus a sack can  
14 contain only cement, or a mixture of cement and CKD, or a  
15 mixture of any other cementitious formulation.

16 Examples of the formulations of three embodiments of  
17 this invention are shown in Table I. Tested hard plugs  
18 produced by this invention in accordance with the  
19 formulations in Table I, meet or exceed API specifications.

20 Table I

21	Formulation	A	B	C
22	Dry cementitious materials:			
23	% cement	40	50	60
24	% CKD	60	50	40
25	Gallons of water per sack:	6.5	8	10

26 Table II illustrates load data of laboratory tested  
27 cores prepared from formulations of this invention, where  
28 CKD and cement from Source I of Table IV have been used to

1 prepare hard cores. Tests of the hard cores in Table II  
2 were conducted in accordance with ASTM C-39 specification.

3 Table II shows that the compressive strengths of cured  
4 samples produced by this invention increases with curing  
5 time. In these examples, the SG of the Type II Portland  
6 cement was 3.14 and the SG of the CKD was 2.8.

7 Yield ("Y") is the cubic feet of slurry produced per  
8 sack of cementitious material after slurring with a  
9 predetermined amount of water. In this case the sack is a  
10 94 lb mixture of cement and CKD. Density of the slurry is  
11 usually expressed in lb/cf. Usually both yield and density  
12 are calculated. The calculated yield is the sum of the  
13 volumes of each component per sack which at ambient  
14 conditions is equal to

$$\begin{aligned} 15 & 0.01506 \times \left( \frac{\% \text{ cement}}{\text{SG cement}} + \frac{\% \text{ CKD}}{\text{SG CKD}} \right) + 0.1337 \times (\text{gal. of water}) \\ 16 & \\ 17 & \text{Eq. 1} \end{aligned}$$

18 The calculated density ("D") is the sum of the weights  
19 of each component per sack divided by the sum of the volumes  
20 of each component per sack, which is equal to

$$\begin{aligned} 21 & (94 \text{ lb} + \{8.337 \times (\text{gal. of water})\}) / Y \quad \text{Eq. 2} \end{aligned}$$

22 Payment is usually based on the number of cubic feet of  
23 slurry used for a well closure operation. Therefore, for a  
24 given load and compressive strength requirement for closure  
25 of a given well, the cementitious slurry which is the  
26 cheapest per cf, while still meeting particular requirements  
27 for the well, is economically advantageous for a well  
28 closure operation. The cementitious slurry which is the

1 cheapest includes the cost of th cementitious composition  
2 from the cement manufacturer, the cost of blending, and the  
3 cost of transportation and off-loading at the off-loading  
4 site. In this invention, however, there is no cost of  
5 blending since blending of the cement and CKD is achieved  
6 automatically during transit from the cement manufacture to  
7 the off-load site. Both sack cost and yield are factors in  
8 determining the cementitious composition cost. This  
9 invention also provides a method of estimating such cost and  
10 markup prices.

11 Table III is an example of the yields and densities of  
12 typical prior art formulations using G Series Portland  
13 cement and silica product as the cementitious materials  
14 which when mixed with water produced a cementitious slurry  
15 which meets API specifications. In this example the SG of  
16 the G Series Portland cement is 3.15 and the SG of the  
17 silica product is 2.65. The bulk density of the G Series  
18 Portland cement is 94 lb/cf and the bulk density of the  
19 silica product is 74 lb/cf. The typical cost per cf of just  
20 the raw ingredients, i.e. exclusive of transportation and  
21 blending, is estimated to range from about \$1.06 to about  
22 \$1.55.

23 Table IV shows the chemical analysis on a major oxide  
24 bases of several typical CKD by different cement  
25 manufacturers. This data was supplied by Sources I, II and  
26 III, and taken from U.S. Patent No. 4,432,800 for Sources  
27 IV, V and VI. Slurries produced by this invention using the  
28 CKD from these sources will meet or exceed API  
29 specifications. Although almost any CKD from any cement  
30 manufacturer can be used in this invention with adjustment  
31 of the cement to CKD ratio, CKD from some sources will be

1 preferred over others depending on the particular chemistry  
2 of the CKD and/or the cost of transportation.

3 There is also provided by the principles of this  
4 invention a method for determining a price for providing a  
5 mixture of CKD and cement to a well site comprising  
6 determining the cost of CKD and cement at a manufacturer's  
7 site, determining the cost of transportation of the mixture  
8 from the same manufacturer's site to an off-load site,  
9 determining the total slurry cost of providing the mixture  
10 of CKD and cement to the off-load site, and determining a  
11 markup price for the mixture off-loaded at the off-load site  
12 as illustrated in FIG. 3.

13 There is also provided by the principles of this  
14 invention a process of forming a blended mixture of CKD and  
15 cement comprising adding CKD to a container suitable for  
16 shipping cementitious materials from a manufacturer's site  
17 to an off-load site, thereafter, adding cement to the same  
18 container on top of the cement at the same manufacturer's  
19 site, and transporting the cementitious materials in the  
20 container to the off-load site while allowing natural  
21 vibration during the transporting to blend the CKD and  
22 cement as illustrated in FIG. 4.

23 There is also provided by the principles of this  
24 invention a process for closing a well comprising providing  
25 a mixture of CKD and cement at a well site, slurring the  
26 mixture of CKD and cement with water, pumping a sufficient  
27 amount of the slurry down the well to fill the well, and  
28 curing the mixture in the well to form a cementitious  
29 competent hard plug in the well as illustrated in FIG. 5.

30 Accordingly, as illustrated in FIG. 6, there is also  
31 provided by the principles of this invention a method of  
32 determining a lowest cost per unit volume of a hydraulic

1 cementitious slurry comprising determining cost of procuring  
2 a cement and a CKD in a predetermined weight ratio of cement  
3 to CKD at and from a cement source. Then determining yields  
4 of hydraulic cementitious slurries formed by slurring a dry  
5 cement-CKD blend having the predetermined weight ratio of  
6 cement to CKD with various amounts of water.

7 Then determining which of the hydraulic cementitious  
8 slurries when cured over a predetermined period of time will  
9 meet or exceed a predetermined specification, and then  
10 determining a hydraulic cementitious slurry having a lowest  
11 cost per unit volume using the dry cement-CKD blend and  
12 which meets or exceeds the predetermined specification.

13 In a further embodiment, the method also includes  
14 determining a cost for supplying the dry cement-CKD blend  
15 from the cement source to an off-load site using the  
16 hydraulic cementitious slurry determined to have the lowest  
17 cost per unit volume and which meets or exceeds the  
18 predetermined specification.

19 In another further embodiment, the method includes  
20 repeating the above determinations for other ratios of  
21 cement to CKD. For example, determining cost of procuring  
22 the cement and the CKD in another predetermined weight ratio  
23 of cement to CKD at and from the same cement source. Then  
24 determining yields of hydraulic cementitious slurries formed  
25 by slurring a dry cement-CKD blend having the new  
26 predetermined weight ratio of cement to CKD with various  
27 amounts of water.

28 Then determining which of the hydraulic cementitious  
29 slurries when cured over a predetermined period of time will  
30 meet or exceed the same predetermined specification, and  
31 then determining a hydraulic cementitious slurry having a  
32 lowest cost per unit volume using the new dry cement-CKD

1 blend and which meets or exceeds the predetermined  
2 specification. At this stage in the method the lowest cost  
3 hydraulic cementitious slurry has been determined for  
4 slurries with two cement-CKD blends from the same sort but  
5 with different ratios of cement to CKD. Unless there are  
6 other factors to consider, the method now calls for  
7 selecting the cement-CKD blend which results in the lowest  
8 cost for producing a hydraulic cementitious slurry which  
9 meets or exceeds the predetermined specification.

10 The method can be repeated for yet another cement-CKD  
11 blend having another ratio of cement to CKD. For example,  
12 three dry cement-CKD blend which are particularly useful are  
13 2/3, 1/1 and 3/2 parts of cement to parts of CKD where the  
14 hydraulic cementitious slurry to be produced is to be used  
15 for closing wells. This invention, however, is not limited  
16 just to the closing of wells and other uses of the hydraulic  
17 cementitious slurries of this invention can of course be  
18 used for different purposes. Such other purposes can have  
19 different specifications for the resulting cured product.

20 While the preferred embodiments of the present  
21 invention have been described, various changes, adaptations  
22 and modifications may be made thereto without departing from  
23 the spirit of the invention and the scope of the appended  
24 claims. The present disclosure and embodiments of this  
25 invention described herein are for purposes of illustration  
26 and example and modifications and improvements may be made  
27 thereto without departing from the spirit of the invention  
28 or from the scope of the claims. The claims, therefore, are  
29 to be accorded a range of equivalents commensurate in scope  
30 with the advances made over the art.

TABLE II

MATERIAL BLENDS FOR SP 50 SLURRY MIX

CEMENT	CKD	WATER	DENSITY	COMPRESSIVE STRENGTH IN PSI			YIELD	COST
				24 HOUR	7 DAY	14 DAY		
70%	30%	10	97.41	ND	ND	ND	1.82	\$1.31
60%	40%	6.5	108.14	1310	2740	ND	1.37	\$1.55
60%	40%	7	105.77	1270	2480	ND	1.44	\$1.47
60%	40%	8	102.31	ND	ND	1340	1.57	\$1.35
60%	40%	9	99.39	510	1180	1270	1.7	\$1.24
60%	40%	10	96.88	ND	670	1080	1.83	\$1.16
50%	50%	6.5	107.35	1095	2130	ND	1.38	\$1.33
50%	50%	8	102.32	ND	ND	1240	1.57	\$1.16
40%	60%	7	105.04	ND	ND	1430	1.45	\$1.06
40%	60%	8	101.67	ND	ND	ND	1.58	\$0.98

WATER IS GALLONS PER 94 Lb. SACK

DENSITY IS POUNDS PER CUBIC FOOT

COMPRESSIVE STRENGTH RESULTS - ASTM C 39 TEST

YIELD IS NET VOLUME IN CUBIC FEET FOR GALLONS OF WATER PLUS ONE 94 Lb. SACK

COST IS: COST PER CUBIC FOOT OF SLURRY

ND = NOT DETERMINED

THE CKD UTILIZED FOR ALL RESULTS IN THIS TABLE WAS SUPPLIED BY SOURCE I OF TABLE IV

TABLE III  
APPROVED MATERIALS UTILIZED IN SLURRY MIXES  
PRIOR ART FOR WELL SLURRY MEETING API SPECIFICATIONS

CEMENT	SILICA	WATER	DENSITY	COMPRESSIVE STRENGTH IN PSI	YIELD	COST
50%	50%	8	101.03	MEETS API SPECIFICATIONS	1.59	\$2.32
50%	50%	9	98.23	MEETS API SPECIFICATIONS	1.72	\$2.15

CEMENT TYPICALLY UTILIZED IS G SERIES PORTLAND CEMENT \$75.00 PER TON  
SILICA TYPICALLY UTILIZED IS A 200 MINUS SIEVE SPEC PRODUCT \$82.50 PER TON

THESE SLURRY MIXES MEET API SPECIFICATION OF A HARD PLUG OF 1000 PSI COMPRESSIVE STRENGTH

COST IS: COST PER CUBIC FOOT OF SLURRY



TABLE IV  
TYPICAL CHEMICAL ANALYSIS FOR CEMENT KILN DUSTS

SOURCE OF CKD INGREDIENT	CEMENT KILN DUST SOURCE					
	I %	II %	III %	IV %	V %	VI %
SiO <sub>2</sub>	12.3	17.19	17.61	9.9	22.4	14.6
Al <sub>2</sub> O <sub>3</sub>	3	4.34	4.25	3.1	10	3.4
Fe <sub>2</sub> O <sub>3</sub>	1.3	2.13	1.48	1.2	4.1	2.2
CaO	52.6	43.49	62.49	47.6	19.4	46.5
MgO	1.4	0.7	1.18	1.3	0.6	2
SO <sub>3</sub>	3.7	1.34	8.79	0.9	10.1	5
Na <sub>2</sub> O	0.1	0.43	ND	0.1	0.9	0.9
K <sub>2</sub> O	2.4	1.44	2.86	1.1	14.1	5.1
LOSS ON IGNITION	23.3	29.6	ND	31.6	13.2	21.4
FREE LIME	16.9	ND	ND	ND	ND	ND

SOURCES IV, V, AND VI ARE EXAMPLES OF CKD WITH LARGE VARIATIONS OF  
SiO<sub>2</sub> AND CaO AS REPORTED IN U.S. PAT. NO. 4,432,800. THESE VARIATIONS  
DO NOT PRECLUDE THEIR USE IN THIS INVENTION.

FREE LIME: IDENTIFIED SEPERATLY IN CHEMICAL ANALYSIS BUT INCLUDED IN TOTAL  
FOR CaO.

ND = NOT DETERMINED